Effect of urea as pore-forming agent on properties of poly(vinylidene fluoride-co-hexafluoropropylene)-based gel polymer electrolyte

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HIGHLIGHTS

- P(VDF-HFP)-based GPE using urea as pore-forming agent was prepared by phase inversion method.
- The GPE with 0.6 g urea show the smoothest surface morphology with ionic conductivity at room temperature about 2.671 mS cm^{-1}.
- Mechanism of ionic conductivity follows Arrhenius relationship and interfacial performance gains much improvement.
- The assembled Li/GPE/LiCoO$_2$ coin cell shows good rate and cycle performance.

GRAPHICAL ABSTRACT
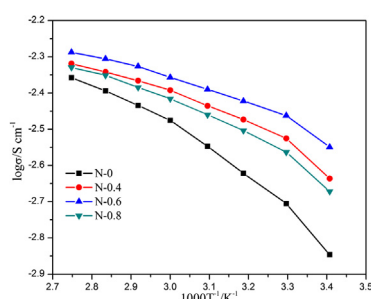
ABSTRACT

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP))-based gel polymer electrolyte (GPE) membranes are prepared by phase inversion method using urea as pore-forming agent and dimethylformamide as solvent, respectively, and the desired polymer electrolytes are obtained after being immersed the as-prepared polymer electrolyte membranes into liquid electrolytes for 1 h. Physicochemical properties of the GPEs are investigated by SEM, XRD, FT-IR, TG-DSC, EIS and LSV. When the weight ratio of urea to P(VDF-HFP) is up to 0.6:4, the results show that the polymer electrolyte membrane presents the most uniform surface with abundant interconnected micro-pores and excellent thermal stability, in which the ionic conductivity at room temperature can reach 2.671 mS cm^{-1} and the reciprocal temperature dependence of ionic conductivity follows Arrhenius relationship. The interfacial resistance of the Li/GPE/Li simulated cell with 0.6 g urea can rapidly increase to a steady value about 650 Ω cm^{-1} from the initial value about 475 Ω cm^{-1} during 15 days storage at 30 °C. The polymer electrolyte with 0.6 g urea can be stable at 5.3 V (vs Li/Li$^+$) at room temperature and the assembled Li/GPE/LiCoO$_2$ coin cell can also show good rate and cycle performance.

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1. Introduction

Recently, more and more attention has been focused on the gel polymer electrolytes (GPEs) for their potential applications in lithium ion battery owing to their lack of leakage, high flexibility and good interfacial compatibility with electrodes [1,2]. It is worthy to note that the safety performance of the lithium ion battery with GPEs gains much improvement because the GPEs with few free-flowing liquid electrolytes can prevent combustions and explosions from decomposition of the liquid electrolytes in some extreme conditions. Generally, GPE is mainly composed of polymer matrix, entrapped liquid electrolytes and suitable additives. Among the numerous polymer matrices studied, the copolymer of vinylidene fluoride and hexafluoropropylene (P(VDF-HFP)) is considered

to be the most potential matrix material, because it has relatively lower crystallinity due to the copolymerization effect between VDF and HFP in comparison with poly(vinylidene fluoride) (PVDF) [3–5]. In addition, HFP amorphous phase can facilitate high ionic conduction and VDF crystalline phase can act as a mechanical support for the polymer electrolytes [5]. The mainstream preparation method of GPEs is phase inversion technique, mainly including the processes of fabricating and activating the porous polymer electrolyte membranes [6,7]. It is well known that the more the micro-pores are, the higher the electrolyte uptake ratio is. In other words, the rich micro-pores can enhance the ionic conductivity of the polymer electrolytes. Therefore, fabricating polymer electrolyte membranes with porous structure becomes the focal topic in the field of the polymer electrolytes for lithium ion battery. Since the supercritical carbon dioxide was successfully used to prepare porous polymer membrane, more and more pore-forming agents, such as polyvinyl pyrrolidone, polyethylene glycol and salicylic acid, are employed to enhance ionic conductivity of polymer electrolytes by improving the micro-pore structure of the porous polymer membranes [4,8–11]. Urea, easily decomposing into carbon dioxide and ammonia gas at increasing temperature, is a novel pore-forming agent to fabricate porous polymer electrolyte membranes [12]. However, some properties reported by Chen, such as thermal stability and electrochemical working window, decrease with adding urea into polymer electrolyte membranes, while the ionic conductivity and interfacial stability gain improvement, which can be attributed to the poor mechanical properties of the copolymer matrix P(AN-MMA-ST) [13]. In the present work, P(VDF-HFP) is selected as polymer matrix to fabricate the polymer electrolytes using urea as pore-forming agent. The physicochemical properties, such as thermal stability, electrochemical working window, ionic conductivity, interfacial stability and surface morphology of the polymer electrolyte membranes, and the battery performance are investigated. And the results indicate that urea can be an excellent pore-forming agent to fabricate the polymer electrolyte membrane for the lithium ion battery.

2. Experimental

2.1. Preparation of GPEs

The P(VDF-HFP)-based polymer electrolyte membranes were prepared by the standard solution-casting technique in this work. The materials used were P(VDF-HFP) (Atofina, Kynar Flex, 12 wt.% HFP) and 1.0 M LiPF$_6$-ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1:1:1, $v/v/v$, Dongguan Shanshan Battery Materials Co., Ltd.). Prior to use, P(VDF-HFP) was dried under vacuum at 60 °C for 24 h. Urea and N,N-dimethylformamide (DMF) (A.R., Sinopharm Chemical Reagent Co., Ltd.) were used as pore-forming agent and solvent, respectively. Urea and P(VDF-HFP) mixture with different weight ratios, namely 0:4, 0.4:4, 0.6:4 and 0.8:4, were added accordingly and dissolved in DMF. The mixed solution was continuously stirred at 40 °C to obtain homogeneous casting solution, and then the solution was cast onto a glass plate with a doctor blade to form the wet membrane, the dry and porous membrane with the thickness about 120 μm was obtained by phase inversion technique after being dried in a vacuum oven at 120 °C for 10—12 h. The desired polymer electrolytes were achieved by being soaked the as-prepared circular polymer electrolyte membranes (18 mm × 0.12 mm) into the 1.0 M EC/DMC/EMC liquid electrolytes solution at room temperature for 1 h in the argon-filled glove box. For the sake of convenience, the as-prepared GPEs are labeled as N-x, in which x represents the adding amount of urea in the polymer electrolyte system.

2.2. Properties characterizations

The morphology and microstructure of P(VDF-HFP)-based polymer electrolyte membranes with different contents of urea were examined using a scanning electron microscope (SEM, JEOL JSM6301F). The X-ray diffraction (XRD, Rint-2000, Rigaku) using CuKα radiation ($\lambda = 0.15406$ nm) in the range of $2\theta = 5—60°$ was employed to identify the crystalline phase of the as-prepared polymer electrolyte membranes. Fourier transform infrared (FT-IR) spectra were used to confirm the structure of the as-prepared GPEs on Nicolet 6700 instrument with a wave-number resolution of 2 cm^{-1} in the frequency of 4000—400 cm^{-1}. Thermogravimetry and differential scanning calorimeter (TG-DSC) measurements of the polymer electrolyte membranes were carried out on a Perkin—Elmer Pyris-1 analyzer with a heating rate of 10 °C min^{-1} from 20 to 400 °C. A flow of argon gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. The ionic conductivity of the blocking stainless steel (SS)/As-prepared electrolytes/SS model cells was determined at various temperatures (293—363 K, the cells were thermostated during measurements) by electrochemical impedance spectroscopy (EIS, CHI660b) with Ac amplitude of 10 mV from 10^5 to 0.01 Hz. Electrochemical working window of the Li/As-prepared electrolytes/SS asymmetrical cell was measured by running linear sweep voltammetry (LSV). The LSV tests were carried out using the same system as that in EIS at a scanning rate of 5 mV s^{-1} from 2.0 to 6.8 V. In addition, the interfacial properties between the electrolyte and the electrodes were studied by investigating the resistance change of the Li/As-prepared electrolytes/Li symmetrical cell at 30 °C with different storage times. The charge—discharge tests of the Li/GPEs/LiCoO$_2$ 2032 coin cells were carried out using Land Battery Test System (Wuhan Land Electronic Co., Ltd. China). The electrode formulation consisted of 80 wt.% LiCoO$_2$ (Dongguan Shanshan Battery Materials Co., Ltd.), 10 wt.% carbon black, and 10 wt.% PVDF. The charge—discharge cycling was performed at different current densities with cut-off voltages of 2.75—4.25 V at room temperature.

3. Results and discussion

3.1. Surface morphology

SEM images of different polymer electrolyte membranes are shown in Fig. 1. It is obviously observed that the surface morphology varies with various contents of added urea. Compared with pure P(VDF-HFP) membrane displayed in Fig. 1(A), the membranes with urea have more interconnected micro-pores, which suggests that the membranes can entrap more liquid electrolytes and provide more Li$^+$ transferring passageways, and hence may show higher ionic conductivity. When the membranes are subjected to vacuum drying, the added urea begins to decompose into ammonia gas and carbon dioxide and then form micro-pores in the membranes. It is obviously observed from Fig. 1 that the amount of the micro-pores in polymer electrolyte membrane becomes more with increasing the added amount of urea, however the variation trend of the pore-size is much different, in which the pore-size firstly reaches a maximum and then decreases in the same condition. It is generally known that only abundant micro-pores with appropriate pore-size can entrap more liquid electrolytes without weakening the mechanical properties of the polymer electrolytes. Obviously, the polymer electrolyte membrane with 0.6 g urea presents the smoothest surface and most abundant micro-pores with appropriate pore-size, which may lead to the highest ionic conductivity and best interfacial stability.
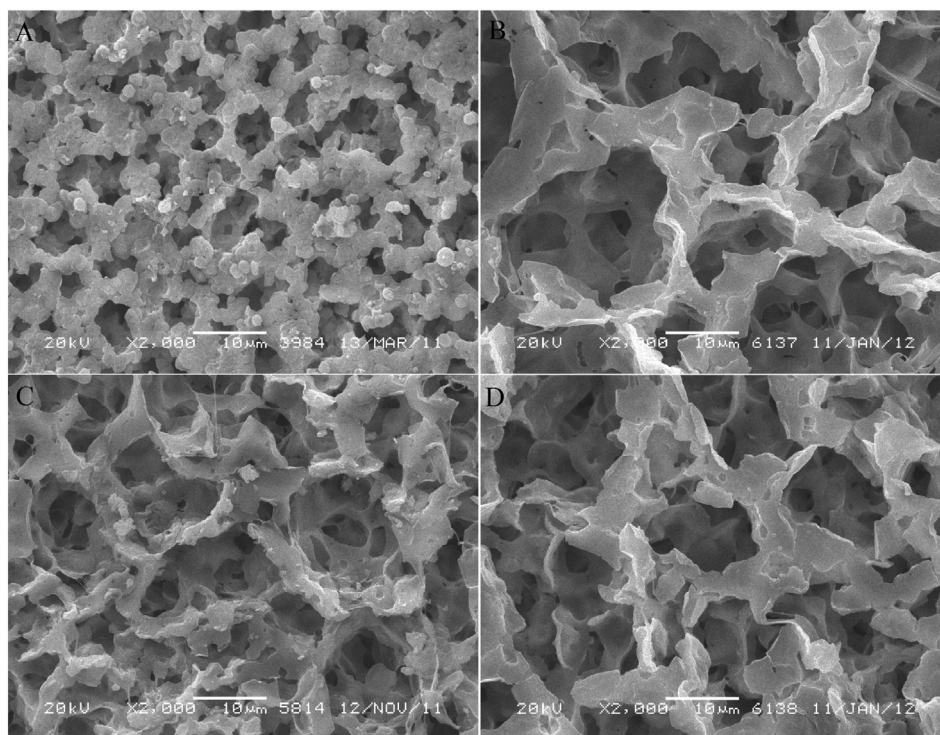
Fig. 1. SEM images of pure P(VDF-HFP) membrane (A) and polymer electrolyte membranes with 0.4 g urea (B), 0.6 g urea (C) and 0.8 g urea (D).

3.2. XRD analysis

XRD patterns of pure urea and polymer electrolyte membranes with different contents of urea are shown in Fig. 2. It is well known that urea is a crystal with perfect crystalline form and P(VDF-HFP) is a semicrystalline copolymer with characteristic diffraction peaks at $2\theta = 18.3, 20.0, 26.6$ and $39.1°$, as demonstrated in Fig. 2 [14]. As displayed in Fig. 2, the polymer electrolyte membranes with urea have similar diffraction patterns, in which the diffraction peaks at $2\theta = 18.3$ and $26.6°$ disappear and the peaks at $2\theta = 20$ and $39°$ become broader and weaker compared with the plot of pure P(VDF-HFP) polymer electrolyte membrane. The results suggest that
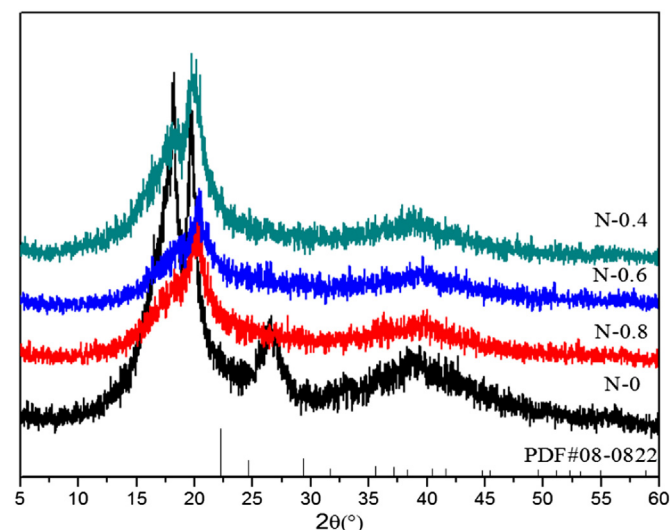
adding urea into polymer matrix can reduce the crystallinity and increase the amorphous areas of polymer matrix, which can enhance ionic conductivity of the polymer electrolytes.

3.3. FT-IR analysis

To investigate the interaction between urea and polymer matrix P(VDF-HFP), the FT-IR spectra was employed to confirm the structure of the polymer electrolytes with urea. It is obviously observed from Fig. 3 that the characteristic absorption peaks of urea and polymer electrolyte with 0.6 g urea are 662 (A) and 1670 cm^{-1} (B), which can be attributed to the asymmetric stretching vibration of −C−F from P(VDF-HFP) polymer and stretching vibration of amino group from urea, respectively. It is worthy to note that the absorption bands around 1670 cm^{-1} (B) in Fig. 3(b) get narrower and stronger compared to the one in Fig. 3(a), which can be assigned to the vibration of C=C double bond from the matrix and the new −C−N bond from the interaction between the polymer matrix and urea. Moreover, new absorption peaks around 2933 cm^{-1} (C) in Fig. 3(b) appear, which can be attributed to the −F−CO−N bond from the interaction between the amino group and F atom. These results may provide reasonable evidences that the urea is not only used as pore-forming agent to improve the porous membrane structure, but also interacts with the polymer matrix to fabricate the polymer electrolytes during the preparation process.

3.4. Ionic conductivity

Ionic conductivity is considered to be the most important parameter to evaluate the practical applications for lithium ion battery. The plots about variation of ionic conductivity with temperature are demonstrated in Fig. 4. The curves of ionic conductivity have similar rising tendency with increasing temperature and the curves of the polymer electrolytes with urea are always above the one without urea. As shown in Table 1, the ionic conductivity at
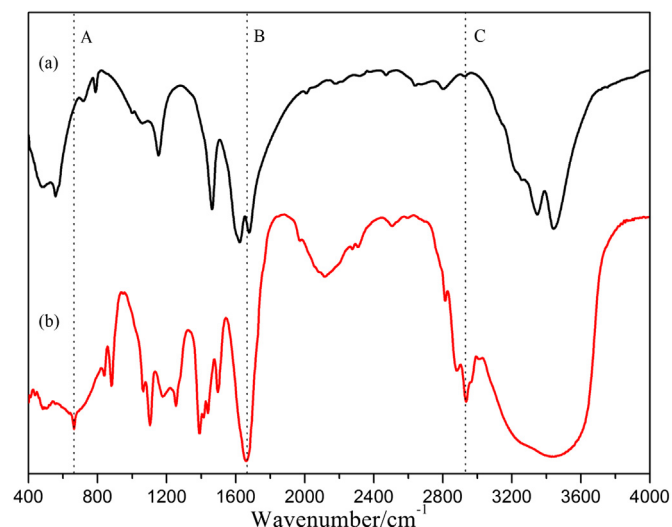

Fig. 2. XRD patterns of pure urea and different polymer electrolyte membranes.

Fig. 3. FT-IR spectra of pure urea (a) and polymer electrolyte membrane with 0.6 g urea (b).
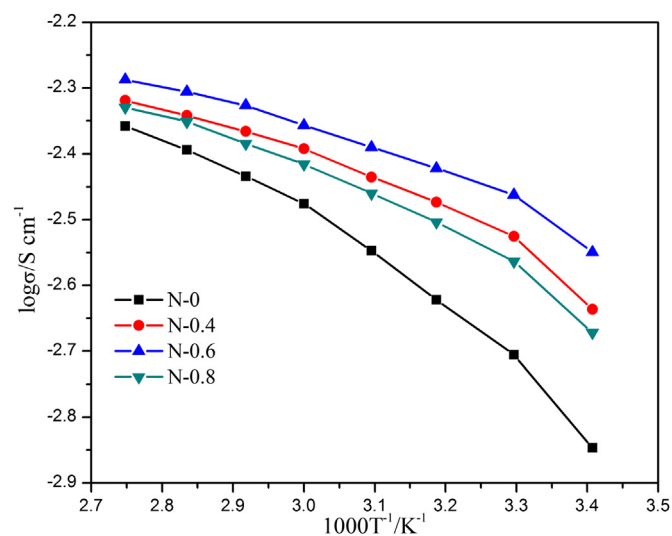

Fig. 4. Reciprocal temperature dependence of ionic conductivity of different polymer electrolytes.

ambient temperature of the polymer electrolytes with different contents of urea is 2.178, 2.671 and 1.928 mS cm^{-1}, respectively. However, the ionic conductivity of pure P(VDF-HFP) polymer electrolyte is only 1.172 mS cm^{-1}, indicating that adding urea into polymer electrolyte can enhance ionic conductivity. Furthermore, it can be found from Fig. 4 that the logarithm of ionic conductivity is approximately linear with reciprocal temperature, suggesting that the mechanism of ionic conduction in the polymer electrolyte system may obey to Arrhenius relationship demonstrated in the

Table 1
Ionic conductivity, crystallinity and activation energy of different polymer electrolytes.

Sample	σ/mS cm^{-1}	x/%	E_a/kJ mol^{-1}
N-0	1.172	100.0	8.325
N-0.4	2.178	57.34	6.138
N-0.6	2.671	49.78	5.332
N-0.8	1.928	61.46	6.456

following Eq. (1), where E_a, R and T refer to the activation energy for ionic transportation, gas constant and temperature, respectively [6,15,16]. E_a of the different polymer electrolytes with ionic conductivity at room temperature is listed in Table 1.

$$\sigma = \sigma_0 e^{-E_a/RT} \tag{1}$$

As shown in Table 1, the lower the value of activation energy is, the higher the value of ionic conductivity is, in which the polymer electrolyte with 0.6 g urea has the highest ionic conductivity at room temperature about 2.671 mS cm^{-1} with the lowest activation energy about 5.332 kJ mol^{-1}. This phenomenon can be attributed to the increasing temperature and added urea. On one hand, increasing temperature can intensify thermal motion of polymer molecular and hence decrease ionic transferring energy, in other words, the increasing temperature can enhance ionic conductivity by decreasing the ionic transferring energy [17]. On the other hand, the formation of hydrogen bonds ascribed to the fluorine groups (−F) of polymer matrix and carbonyl (C=O) and amino group (−NH$_2$) of urea and the Lewis acid−base interaction between the fluorine anions (F$^-$) of P(VDF-HFP) and lithium cations (Li$^+$) of lithium salt can form more amorphous areas to enhance ionic conductivity [12]. In addition, the fully interconnected micro-pores in the polymer electrolyte membranes can entrap more liquid electrolytes and also provide more extra passageways for Li$^+$ migration.

3.5. Thermal analysis

Fig. 5 presents the TG (A) and DSC (B) curves of the polymer electrolyte membranes with different amounts of urea. It can be derived from Fig. 5(A) that the thermal decomposing temperature of the pure P(VDF-HFP) polymer membrane is about 340 °C and the one of the polymer electrolyte membrane with 0.6 g urea is up to 375 °C. With the content of urea increasing to 0.6 g, the thermal decomposing temperature increases progressively, indicating that the polymer electrolyte membranes with urea become more and more stable. The results indicate that there may be some interaction between the polymer matrix and urea to fabricate the more stable polymer electrolyte, which was confirmed by FT-IR analysis. However, the thermal decomposing temperature decreases dramatically when the amount of added urea continues to increase, which is attributed to the decomposition in advance of urea aggregated on the surface of the membrane. Fig. 5(B) presents the DSC curves of the polymer electrolyte membranes. According to the following relationship $x\% = \Delta H_f/\Delta H_{mf}^{\ominus}$ (where, $\Delta H_{mf}^{\ominus}$ is the standard enthalpy of fusion of pure PVDF polymer electrolyte membrane, 104.7 J g^{-1}, and ΔH_f is the enthalpy of fusion of the P(VDF-HFP)-based polymer electrolyte membrane), the crystallinity of the polymer electrolyte membranes with ionic conductivity at room temperature is calculated and listed in Table 1 [15,18]. It is obviously observed that the polymer electrolyte membrane with N-0.6 urea has minimum crystallinity about 45.78%, which is consistent with the results of XRD analysis and further confirms the positive role of appropriate content of urea.

3.6. Electrochemical working window

The electrochemical working window of the assembled Li/GPEs/SS asymmetric model cells is investigated using the LSV tests and the corresponding LSV plots are shown in Fig. 6. It is obviously observed from Fig. 6 that the electrochemical working window of the pure P(VDF-HFP) polymer electrolyte is about 4.5 V, which is consistent with the result reported in the literature [19]. The electrochemical working window of the polymer electrolytes with urea is higher than that of the pure P(VDF-HFP) polymer
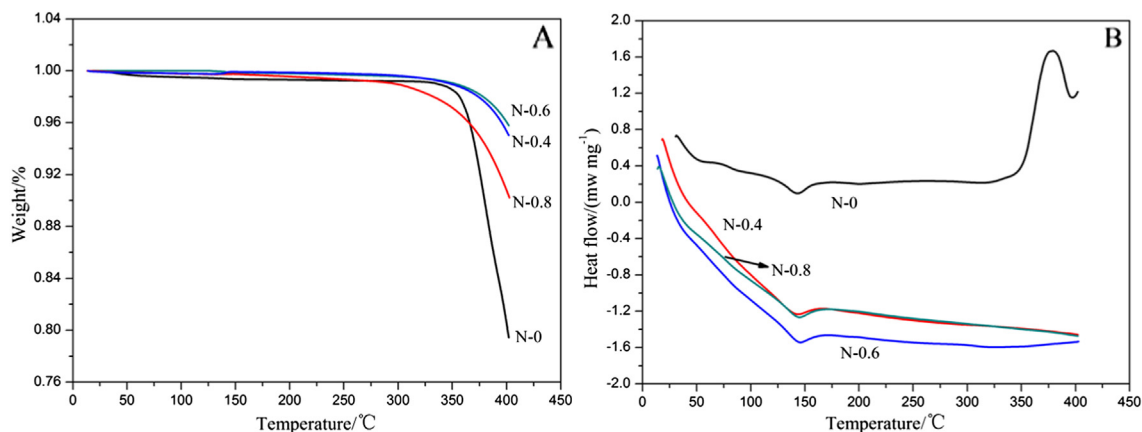
Fig. 5. Plots of TG (A) and DSC (B) about polymer electrolyte membranes with and without urea.

Fig. 6. LSV plots of Li/GPEs/SS cells with different polymer electrolytes.

electrolyte, which can be attributed to the interaction between P(VDF-HFP) matrix and urea. It is worth noting that the electro-chemical working window of the polymer electrolyte with 0.6 g urea can be up to 5.3 V, which is acceptable for the practical lithium ion battery.

3.7. Interfacial stability

The interfacial stability between the electrodes and the electrolyte was studied by monitoring the impedance variation of the assembled Li/GPEs/Li symmetrical cell at various storage times at 30 °C. Fig. 7 displays the typical Nyquist impedance plots of the symmetric model cell measured for 15 days storage at 30 °C. It is obviously observed from Fig. 7 that the impedance plots are characterized by one semicircle in all the frequency range. The plots can be fitted using the equivalent circuit described as R_b in series with parallel (CPER_{ct}) ele-ments {R_b(CPER_{ct})} demonstrated in the inset of Fig. 7, in which R_b is attributed to the bulk resistance of polymer electrolyte, R_{ct} is the interfacial resistance and CPE is the capacitance of the interfacial layer [20]. As shown in Fig. 7, the R_b in each plot almost remains a constant during 15 days storage. However, as to R_{ct}, the interfacial impedance of the polymer electrolytes presents obvious differences, in which R_{ct} of the polymer electrolyte with 0.6 g urea starts from about 475 Ω cm^{-1} to end about 650 Ω cm^{-1} after 15 days storage, and R_{ct} of the pure P(VDF-HFP) polymer electrolyte presents the tendency to keep growing with time under the same condition. The results suggest that adding urea into polymer matrix is helpful to improve the interfacial stability between the electrodes and the electrolyte.

3.8. Battery properties

The first charge–discharge curves of the Li/GPEs/LiCoO$_2$ coin cell at room temperature are shown in Fig. 8. It is obviously
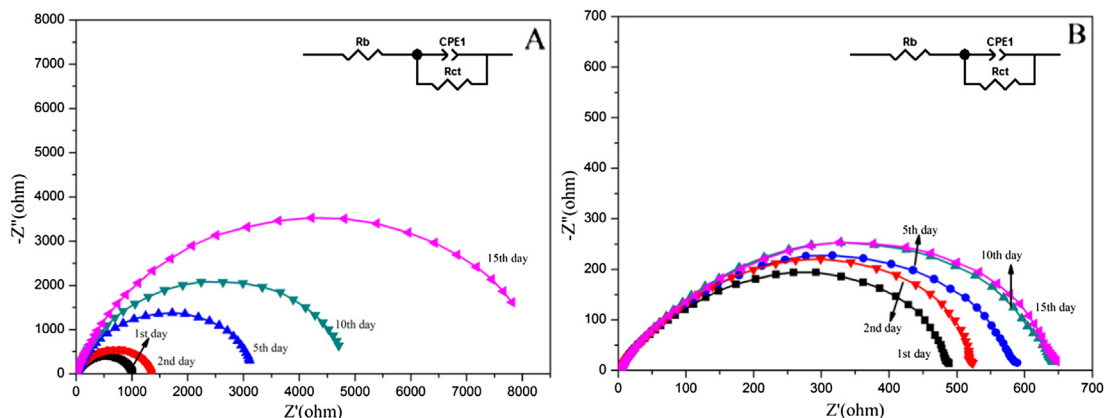

Fig. 7. Nyquist plots of two kinds of Li/GPEs/Li cells with various storage times at 30 °C (A: pure P(VDF-HFP) polymer electrolyte; B: P(VDF-HFP) polymer electrolyte with 0.6 g urea), where the inset shows the equivalent circuit.
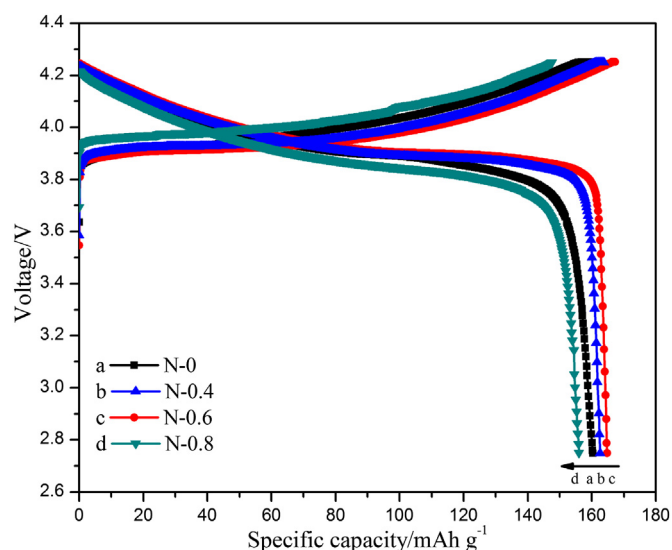
Fig. 8. First charge–discharge curves of Li/GPEs with different contents of urea/LiCoO$_2$ coin cell at room temperature.

Fig. 10. Cycle stability and coulombic efficiency curves of Li/GPE with 0.6 g urea/LiCoO$_2$ coin cell at different rates.

observed that the charge–discharge curves are similar to what is observed in lithium ion battery using commercial polyethylene membrane as separator, which ensures a good contact between the electrodes and the GPEs. The first discharge capacity increases to a maximum and then decreases with increasing the content of added urea. Compared with other curves in Fig. 8, the GPE with 0.6 g urea shows the highest discharge capacity about 164.8 mAh g^{-1}, which suggests that adding appropriate urea into polymer electrolytes can improve the first charge–discharge capacity of lithium ion battery.

The discharge curves of Li/GPE with 0.6 g urea/LiCoO$_2$ coin cell at room temperature at different rates are displayed in Fig. 9 (0.1C, 0.2C, 0.5C, 1.0C and 2.0C). It can be seen from Fig. 9 that the discharge capacity of the cell gradually fades with increasing discharge rate, but still keeps relatively high capacity value. The cell using the polymer electrolyte with 0.6 g urea achieves a high capacity about 164.8 mAh g^{-1} at 0.1C and 152.2 mAh g^{-1} at 0.5C. And at 2.0C, the capacity also keeps 81.78% of that at 0.1C for the cell,
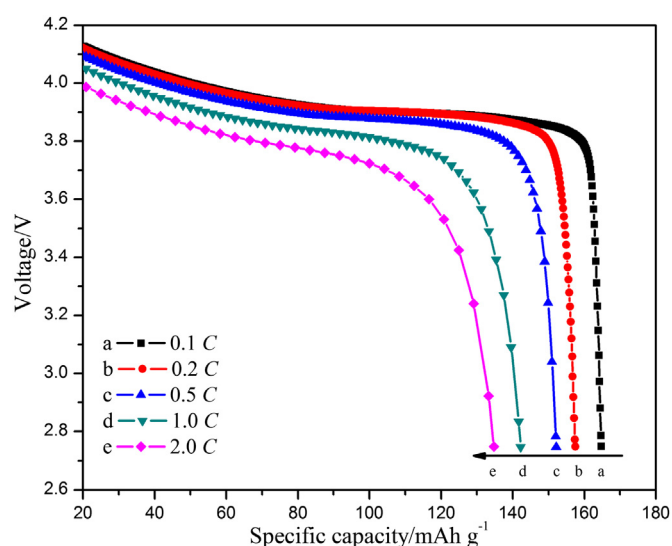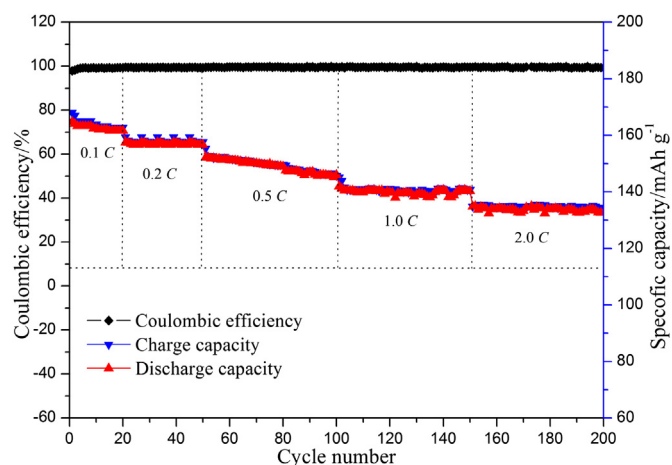
which indicates that the cell using this polymer electrolyte shows excellent rate properties.

The cycle stability and coulombic efficiency curves of the Li/GPE with 0.6 g urea/LiCoO$_2$ coin cell at different rates (0.1C, 0.2C, 0.5C, 1.0C and 2.0C) are demonstrated in Fig. 10. It is evident from Fig. 10 that the coulombic efficiency of the cell with the polymer electrolyte in all the test range keeps at about 100% and the discharge capacity fades slowly at different rates. It is obviously observed from Fig. 10 that the cell with the GPE can keep high discharge capacity about 152.2 mAh g^{-1} at 0.5C after 50 cycles, which is about 92.36% capacity retention ratio of the cell at 0.1C. Moreover, the cell still can reach 134.8 mAh g^{-1} at 2.0C after 200 cycles. The results show that the cycle stability and coulombic efficiency of the cell using the GPE with 0.6 g urea gain much improvement, which may be attributed to the improved interfacial stability and ionic conductivity.

4. Conclusions

P(VDF-HFP)-based gel polymer electrolytes using urea as pore-forming agent are successfully fabricated by phase inversion method. Different contents of urea have great impact on physico-chemical and electrochemical performance of the polymer electrolytes. It is found that the use of 0.6 g urea in the formation of P(VDF-HFP)-based GPEs can well improve the micro-pore structure of the polymer electrolyte membranes and thus enhance the ionic conductivity of the GPEs with excellent thermal and interfacial stability. Furthermore, the assembled Li/GPE/LiCoO$_2$ coin cell shows good rate and cycle performance, which can ensure it to be the most potential candidate as polymer electrolyte for lithium ion battery.

Fig. 9. Rate performance of Li/GPE with 0.6 g urea/LiCoO$_2$ coin cell at room temperature.

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